

## ELECTRONICS APPLICATIONS OF RESONANCE IMAGING

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## INTRODUCTION

Non-metallic materials are important in a wide variety of applications in the manufacture of semiconductor components and packages. The nondestructive evaluation of flaws and defects in non-metallic materials including polymers, semiconductors and ceramics used in this industry is a high priority for scientists and engineers involved in the manufacture of microelectronic circuits. Magnetic resonance imaging techniques are potentially quite powerful tools for this application; however, progress in this area has been slowed significantly by the strong magnetic interactions present in solid materials. Techniques that have been developed for resonance imaging focus on solving the problem of poor resolution caused by intrinsically broad resonance lines in solids through modifications of NMR techniques that artificially narrow the resonance line, or by the use of paramagnetic resonance to investigate signals created only by damage sites together with data reduction methods permitting deconvolution of narrow spectral features from wide lines. These imaging techniques have potential application to such packaging problem areas as the curing phenomena in polymeric materials, adhesion and delamination in composites and sintering of ceramic materials. Promising applications in the semiconductor manufacture process include quantifying the number and location of impurities in wafers, determining the damage levels and degree of annealing needed in the ion implantation process, and ascertaining damage in a semiconductor subjected to such processes as reactive ion etching.

The ability to examine the internal structure of polymers, ceramics and semiconductors for impurities, defects and other flaws is of great significance in the control of semiconductor manufacturing. A wide variety of analytical techniques have been used to examine materials in these categories including: X-ray analysis, photothermal imaging, ultrasonics, scanning electron microscopy, and others. All, however, suffer from some basic limitations when applied to the wide variety of materials used in integrated circuits. X-ray techniques are relatively limited when examining low atomic number and low density species such as polymers and ceramics, and also suffer from poor contrast. Photothermal techniques are typically of greatest utility only in measurements where limited penetration such as associated with studies of coatings or other thin film structures are required. Ultrasonic techniques provide a large penetration

depth, but three-dimensional images of defects or damage in the materials are only obtained with great difficulty. Typical scanning electron microscopy is, of course, useful only at the surface of materials such as semiconductors. Using a method such as electron paramagnetic resonance imaging provides the potential for nondestructive measurement of bulk ceramics, polymers and semiconductors with true three-dimensional images of defects and impurities in these materials. Our work shows that in all three classes of materials, magnetic resonance imaging is plausible using resonance effects that are intrinsic to the materials or alternately by introducing paramagnetic penetrants in specimens where appropriate.

## BACKGROUND

Magnetic resonance is the result of the interaction of magnetic moments in a solid with a radio frequency field in the presence of a constant magnetic field. The magnetic moments in the sample may be either nuclear moments residing on certain nuclei as in the case of nuclear magnetic resonance or paramagnetic moments resulting from unpaired electrons. The applied magnetic field induces a splitting of the energy levels of the magnetic moment (the so-called Zeeman effect) with the splitting of the levels increasing linearly with magnetic field. The radio frequency field incident on the sample induces transitions between magnetic states at resonance when the appropriate relation between magnetic field strength and radio frequency field is achieved. The resonance is detected as a peak in the power absorption of the sample as the magnetic field is varied. The intensity of an absorption peak in a uniform magnetic field can be related to the number density of magnetic moments in the sample volume. The peak position in magnetic field and the width of that resonance peak are determined by the chemical and physical environment. When the test sample is placed in a magnetic field that is not spatially uniform, but also contains gradients in that field in the principal coordinates the resonance parameters becomes sensitive to the position of the magnetic moments in the sample. Analysis of such results in the presence of spatially varying magnetic fields is the basis of magnetic resonance imaging which was first discovered by Lauterbur using nuclear resonance techniques. [1]

In the case of electron paramagnetic resonance (epr), specimens must contain paramagnetic resonance active species which contain unpaired electrons. In the case of polymers and other organic materials, broken bonds or other stable-free radicals are active paramagnetic species. In the case of inorganic materials species such as vacancies, impurity atoms, or ions, including transition metals or rare earths in substitutional or interstitial sites and trapped electron hole centers, can all be active paramagnetic species. In attempting to apply magnetic resonance to polymer materials the specific epr active species result from broken bonds, free radicals and the incomplete curing of epoxies. In the case of ceramic wafer materials used in packaging the impurities and defects can be detected and imaged. For semiconductor materials and structures the defects, impurities and various damage sites are potentially active paramagnetic species which can be imaged.

## EPR IMAGING

The electron paramagnetic resonance imaging (epri) technique is based on the localized change of the epr spectrum of a sample caused by the application of magnetic field gradients. The spatial differences in the spectrum caused by the magnetic field gradient results from an inhomogeneous distribution in the number density of magnetic species in the specimen along the gradient direction.<sup>2</sup> If the sample is rotated about the gradient axis or equivalently the gradient is rotated about the sample, mathematical projections of the damage site can be generated. These indi-

vidual slices of spin density along an axis of the specimen can be used to reconstruct two- or three-dimensional images of paramagnetic defects or impurities in the material.

Epr spectra in images were obtained using a Varian E-12 X-band epr spectrometer. The magnetic field distribution was modified from the standard uniform dc magnetic field by adding additional coils to provide magnetic field gradients of the basic uniform magnetic field. Linear magnetic field gradients perpendicular to the sample were produced using counter wound Helmholtz coils while magnetic field gradients perpendicular to the dc field axis were applied using a set of Lewis coils. Data was acquired and analyzed using an HP 9816 computer interfaced to the spectrometer through an HP-1B port. [3]

## IMAGING EXPERIMENTS

To illustrate the technique of resonance imaging, a number of test samples have been investigated consisting of paramagnetic species distributed spatially. The magnetic resonance spectrum associated with any one of these free-radical samples or the combination of them in the absence of a gradient is shown in Fig. 1. The resonance is characterized by a g-factor which gives information as to the nature of the free radical, the linewidth  $\Delta H$  which is reflective of the dynamics of spin relaxation and the integrated intensity which is proportional to the number of spins. Because of the magnetic field modulation and phase sensitive detection used, the first derivative of the absorption is actually displayed (Fig. 1). The effect of an applied field gradient on a spatially distributed sample is to split the spectrum into several peaks each resulting from a spatially resolved individual site of paramagnetic spins. The separation in magnetic field between peaks can be equated to the spatial separation through the known strength of the field gradient. The projection of spin density on the gradient axis is generated by sample rotation. If a series of rotations are carried out, an image of the spin density in the object can be generated.

Generation of spin density profile of an object can be computed using deconvolution techniques. One technique uses the convolution theory of Fourier transforms where the spectrum with the gradient applied is

$$S_g(h) = \int_{-\infty}^{\infty} S_0(h-h')\rho(h')dh' \quad (1)$$

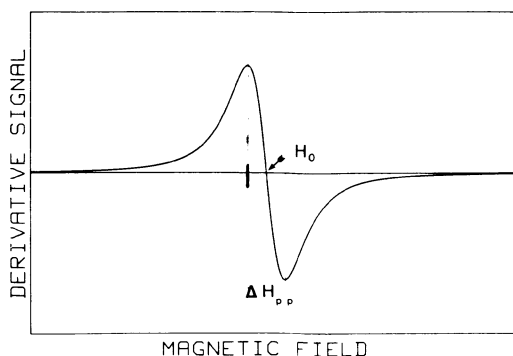


Fig. 1. Epr signal for an ideal free radical with Lorentzian impurities.

where  $S_0(h-h')$  is the spectrum obtained without field gradients and  $\rho(h)$  is the object spin density. The convolution theorem states that the Fourier transform of the spectrum with an applied gradient is equal to the product of the Fourier transforms of the spectrum without the gradient and the spin density. From this it follows that the spin density can be obtained by computing the inverse Fourier transform of the quotient of the Fourier transform of  $S_g(h)$  and  $S_0(h)$ ,

$$\rho(h) = \mathcal{F}^{-1} \left\{ \frac{\mathcal{F}\{S_g(h)\}}{\mathcal{F}\{S_0(h)\}} \right\}. \quad (2)$$

The Fourier transform technique allows computation of complex line shapes as well as removal of the intrinsic linewidths.

The most common image reconstruction from projections algorithm is filtered back projection. This variation of simple back projection or image smearing routine is a two step process. Each projection at angle  $\theta$  is Fourier transformed, low pass filtered and inverse transformed. These modified projections are back projected onto the image plane to generate an image.

#### POLYMERIC SOLIDS

The applicability of electron paramagnetic resonance imaging (epri) as a nondestructive method of determining defects and impurities in electronic materials has been carried out in nylon, either in fiber or rod form. [4-8] An epr signal is generated when chemical bonds in the polymer chains in nylon are broken. When such a bond is broken, unpaired electrons are generated and measured by the epr technique with high sensitivity. Defects in polymers result from either impurities, mechanical damage or damage due to applied radiation. Previously we have reported on the effects of stress in nylon fibers.

More recently the epri technique has been applied to damage in nylon by X-ray radiation in nylon rod localized areas. A test sample consisting of a section of nylon 66 rod approximately 12 mm long was irradiated on two separate sections for 18 hours using  $Cr K\alpha$  radiation. The center section of the rod was shielded from the X-ray radiation over a distance of 7 mm. The epr spectrum of the irradiated nylon with and without a 4 G/mm gradient applied are shown in Fig. 2. The line shape is due to the hyperfine interaction between magnetic nuclei of the polymer and the electron spins. [7,8] There is a significant change in the spectrum of the irradiated nylon with the gradient field applied along the axial direction of the rod. Using the Fourier transform method described, the one-dimensional projection of the spin densities along the axis of the rod was calculated and is plotted in Fig. 3. A significant separation is seen in the longitudinal spin density although the irradiated regions are not totally separated as a result of leakage of the radiation into the shielded area.

#### CERAMIC SOLIDS

Another important class of electronic material are the ceramics used in a variety of multi-layer packaging structures in many integrated circuit applications. The samples studied were high purity fused silica ceramics. The material investigated was slip cast and had a porosity of approximately ten percent. A typical epr spectrum of a ceramic over a wide magnetic field range shows a broad central feature as well as a narrow peak in the low field range near 1700 Gauss (Fig. 6). The g-value or peak position of the resonance results from paramagnetic species in the

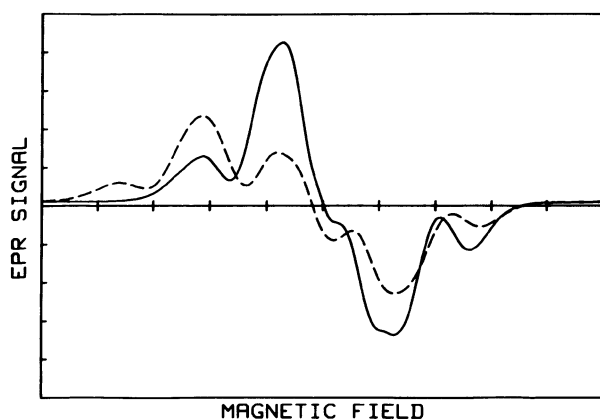


Fig. 2. Spectrum of irradiated nylon with no gradient applied (solid line) and a 4 G/mm gradient (dashed line).

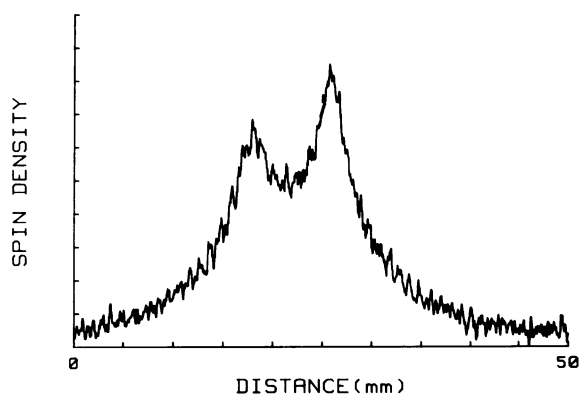


Fig. 3. Projection of spin density for test sample.

material. The central line is at a magnetic field value common for many unpaired electronic species and cannot be identified on this basis alone. The narrow peak at very low field results from an inorganic contaminant in the material.

In order to achieve spectral resolution in measurements where imaging is intended, narrow peaks must be used. With this in mind, the spectrum is restricted to a narrow magnetic field scan centered around the magnetic field value of the narrow peak. The epr scan of silica ceramic over that narrow range is illustrated in Fig. 4. When a linear magnetic field gradient of 10 G/mm is applied, there is a broadening of the magnetic resonance line due to an inhomogeneous distribution of sites in the specimen. Specific information can be obtained only by applying a deconvolution technique as described earlier to the spectra. [7,8] Application of the Fourier transform technique to the data shown in Fig. 4 results in a one-dimensional map of the spin density as a function of distance as shown in Fig. 5. There is a prominent peak in the center of the data whose width corresponds to the width of the sample (~3 mm). Superimposed on this general distribution is a narrower structure presumably due to a local concentration of inorganic impurities in the sample. The resolution of this technique is adequate, but somewhat limited by the linewidth of the specific paramagnetic species in the sample.

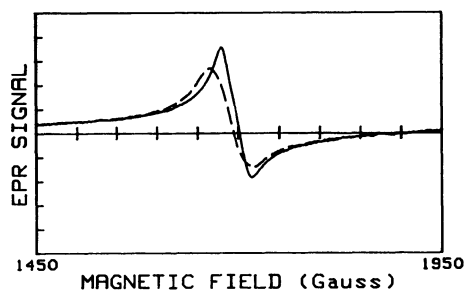


Fig. 4. Epr scan of the silica ceramic over a focused magnetic field region from 1450 to 1950 Gauss. Solid line is spectrum with no gradient; dashed line is with 10 G/mm gradient.

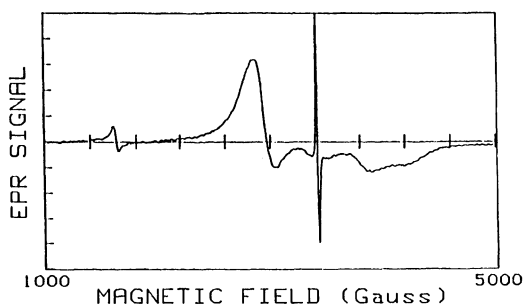


Fig. 5. One-dimensional image of spin density as a function of position in ceramic sample. Image is obtained by using Fourier deconvolution technique on the data of Fig. 4.

Some of the work we previously reported on polymers did employ an organic spin trap to identify damage sites in the material. [5] This substance was diamagnetic and became paramagnetic only when an electron was transferred to it after chemical bonds were broken. In ceramic materials the different chemistry prevents the identical use of a spin trap. There are, however, some organic species such as the DPPH molecule that are paramagnetic and have narrow epr lines. Such organic materials dissolved in solvents can be introduced into the ceramic by simply allowing the solution to permeate the pores of the ceramic medium. Soaking of ceramic samples in a 1 mg/ml solution of DPPH in toluene for a brief period resulted in a total penetration of the substance throughout the ceramic specimen. After the solvent was removed by air drying, the DPPH material coated all of the interior pores of the sample. Inhomogeneities, flaws or cracks in the sample are then visible as a change in spin density at the point of imperfection as a result of the deviation from the uniform distribution of the paramagnetic penetrant. As shown by a broad scan of the high purity fused silica ceramic (Fig. 6) the paramagnetic penetrant DPPH has introduced a very narrow line with a g-value of 2.0. This line is very narrow in comparison to the native spectral features of the ceramic. This work is analogous to experiments on ceramics soaked in water and tested by NMR imaging. [9]

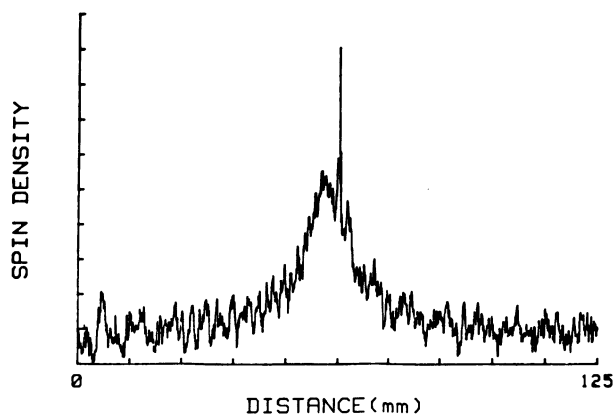


Fig. 6. Epr scan of high purity fused silica ceramic doped with paramagnetic penetrant DPPH. This spectrum has a narrow spectral line superimposed on the spectral features of native material.

A test specimen made up of two pieces of ceramic separated by approximately 2 mm each doped by DPPH [10] were used as a simulation of a large crack in a ceramic sample. The epr spectra obtained with and without the magnetic field along the crack direction can be used to obtain a two-dimensional image of the spin density. The image which is obtained by a filtered back projection method shows a distinct demarcation between the two pieces of ceramic separated by the crack region (Figs. 7, 8). The resolution obtained when this experiment is significantly greater than that which can be obtained using the native epr peaks associated with impurities. Since the procedure itself introduces an impurity in the sample, techniques for removal of the penetrant agent have been investigated. Both heating the sample to 600 °C or soaking in toluene allow removal of the substance from the sample. The efficiency of the removal of the paramagnetic penetrant was determined by measuring the epr spectrum after the cleaning procedure since epr is extremely sensitive to very small amounts of remnant DPPH.

#### SEMICONDUCTORS

A final group of materials which we are currently beginning to explore are the elemental semiconductors which are the predominant active

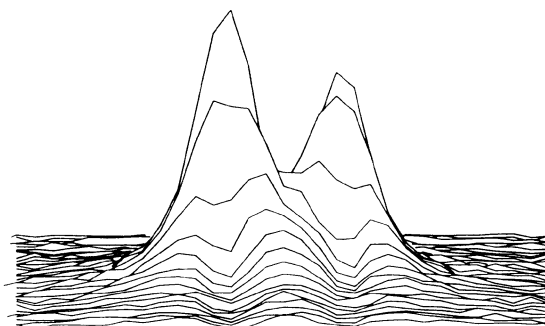


Fig. 7. Image of spin density of test specimen.

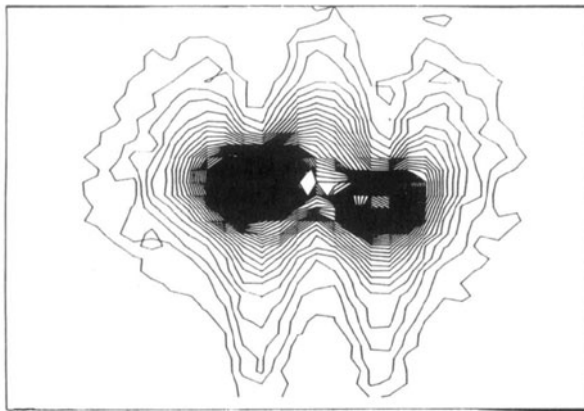


Fig. 8. Contour plot of the image displayed in Fig. 7.

electronic material used today. In general, semiconductors do have substantial numbers of paramagnetic species associated with electrons and impurities which can be used to create a spatial image similar to those described in characterizing distributions of impurity and defect states in polymers and ceramics. As an example, a strong spectrum is associated with impurities in silicon with a resistivity of 0.005 cm yielding a strong narrow line roughly at  $g = 2$  which can be used in spatial imaging. Epr has also recently been used to identify and provide spatial localization of a variety of defects and impurities in gallium arsenide. While the use of epr for defect and impurity identification and localization in these materials has been known for some time, detailed investigations in their use in a noncontact imaging method has not been adequately investigated.

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